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**New Study on Reactions in
Burning Cement
Raw Materials**

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New Study On Reactions In Burning Cement Raw Materials

By L. A. DAHL*

ABSTRACT—

... The ternary system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ involves the three principal oxide constituents of portland cement. The phase diagram is studied with reference to the reactions which occur when ternary cement compositions are burned. Through this study some principles capable of extension to the commercial process of cement manufacture are demonstrated. These include the relation of composition to the proportion of liquid formed in the burning operation, the technical lime limit, and the influence of changes in composition on retention of clinker coating in the kiln. The influence of the burning and cooling operations on the constitution of cement clinker is discussed briefly.

INVESTIGATION OF THE TERNARY SYSTEM $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ was reported in 1915 by Rankin and Wright.¹ The paper was an outstanding contribution to the chemistry of portland cement, since the investigation was the first study of phase equilibria in the system involving the three major components of portland cement clinker. However, the principal interest to cement chemists at the time was not in phase equilibria at clinkering temperatures, but in the fact that three compounds, tricalcium silicate, dicalcium silicate and tricalcium aluminate, were found to exist in portland cement clinker. The present paper is concerned with interpretation of the phase diagram with reference to the reactions which occur during the clinkering process. The three oxides, lime, alumina and silica, constitute about 90 percent of the total composition of most portland cement clinkers. The components which make up the remaining 10 percent have large effects upon phase relations, and so it cannot

be expected that this study of the ternary system will yield exact quantitative information concerning phase relations in the cement system. However, some general principles may be learned, and these may be understood more readily in a study of a ternary system than in a study of a system involving a greater number of components, requiring the use of a space model. A ternary system of the type under consideration may be represented in a triangular phase diagram. Interpretation of the phase diagram requires application of certain properties of the triangular diagram. These properties must be discussed before we can enter into a discussion of the particular phase diagram under consideration.

Properties of Triangular Diagram

The properties of triangular diagrams which are used in a phase diagram and in its interpretation are properties of all types of plane triangles, scalene, isosceles or equilateral.² However, they have been frequently described as belonging uniquely to equilateral triangles. In this study

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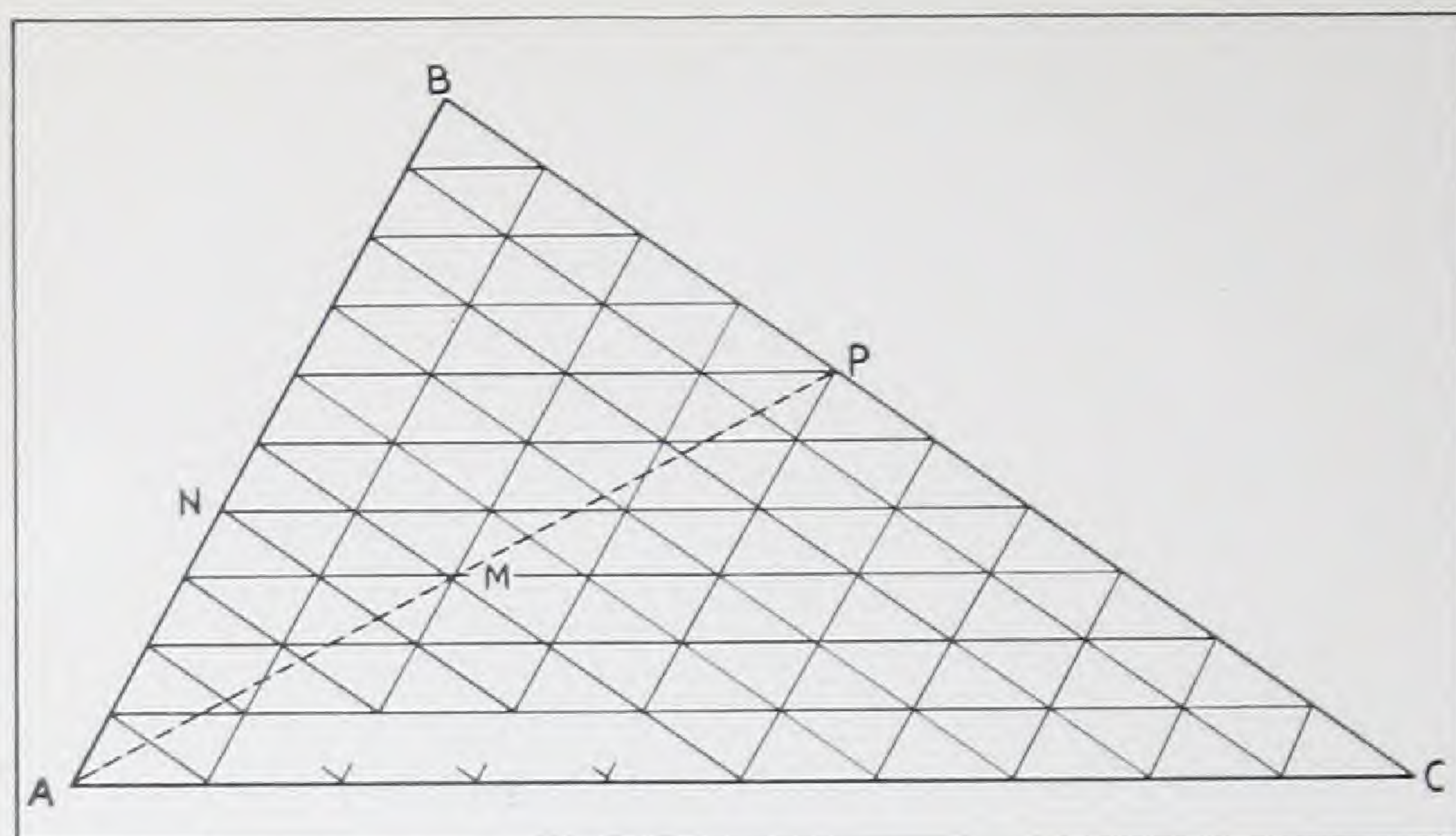


Fig. 1: Triangular diagram of the hypothetical system A-B-C

it will be found convenient at times to connect points representing three co-existing phases by straight lines, and to treat the resulting triangle as a triangular diagram. Such triangles are practically always scalene. This mode of attack will be used repeatedly in the study of the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$. It is therefore deemed advisable to describe the properties of the triangular diagram in such a manner as to avoid the implication that they are limited to equilateral triangles.

The triangle ABC, Fig. 1, represents a ternary system A-B-C. The three sides represent binary systems, A-B, B-C and A-C. Each vertex represents 100 percent of the component indicated. The side opposite a vertex represents zero percent of the component at the vertex. For example, the side AC represents zero percent B. The lines parallel to AC represent percentages of B in 10 percent intervals, from zero to 100 percent. The percentages of A and C are similarly indicated by the lines parallel to the sides BC and AB. The sum of the percentages at any point is 100. For example, M represents 50 percent A, 30 percent B, 20 percent C.

Compositions in a binary system are estimated in a manner similar to that in a ternary system. For example, on the side AB, Fig. 1, which is a binary system, percentages of B are read from the zero point, at A, to the 100 percent point at B. Point N, therefore, represents 40 percent B. Reading in the opposite direction, point N con-

tains 60 percent A, making a total of 100 percent.

A property of the triangular diagram which is frequently found useful is illustrated by the broken line AP in Fig. 1. All compositions on a line drawn from a vertex to the opposite side contain two of the components in the same relative proportions. For example, the percentages of B and C at M are 30 and 20, respectively, a ratio of 3 to 2. At P, the percentages of B and C are 60 and 40, respectively, a ratio of 3 to 2. This is the ratio of B to C at every point on the line AP.

Subdivision of the triangular diagram by lines spaced at equal intervals, such as the 10 percent intervals in Fig. 1, is not actually necessary. The lines parallel to the sides are usually omitted in phase diagrams. It is important, then, to know how to locate the point representing any given composition or, conversely, to determine from the location of any given point the composition it represents. In the case of a binary system, the distances from any given point to the ends of the line represent *relative* proportions of the components, and are converted to fractional weights by dividing each distance by the length of the line. It must be borne in mind that the distances are taken in reverse order. For instance, the relative proportions of A and B in N are the distance of N from B and A, respectively. In showing only a portion of a phase diagram it is sometimes convenient to

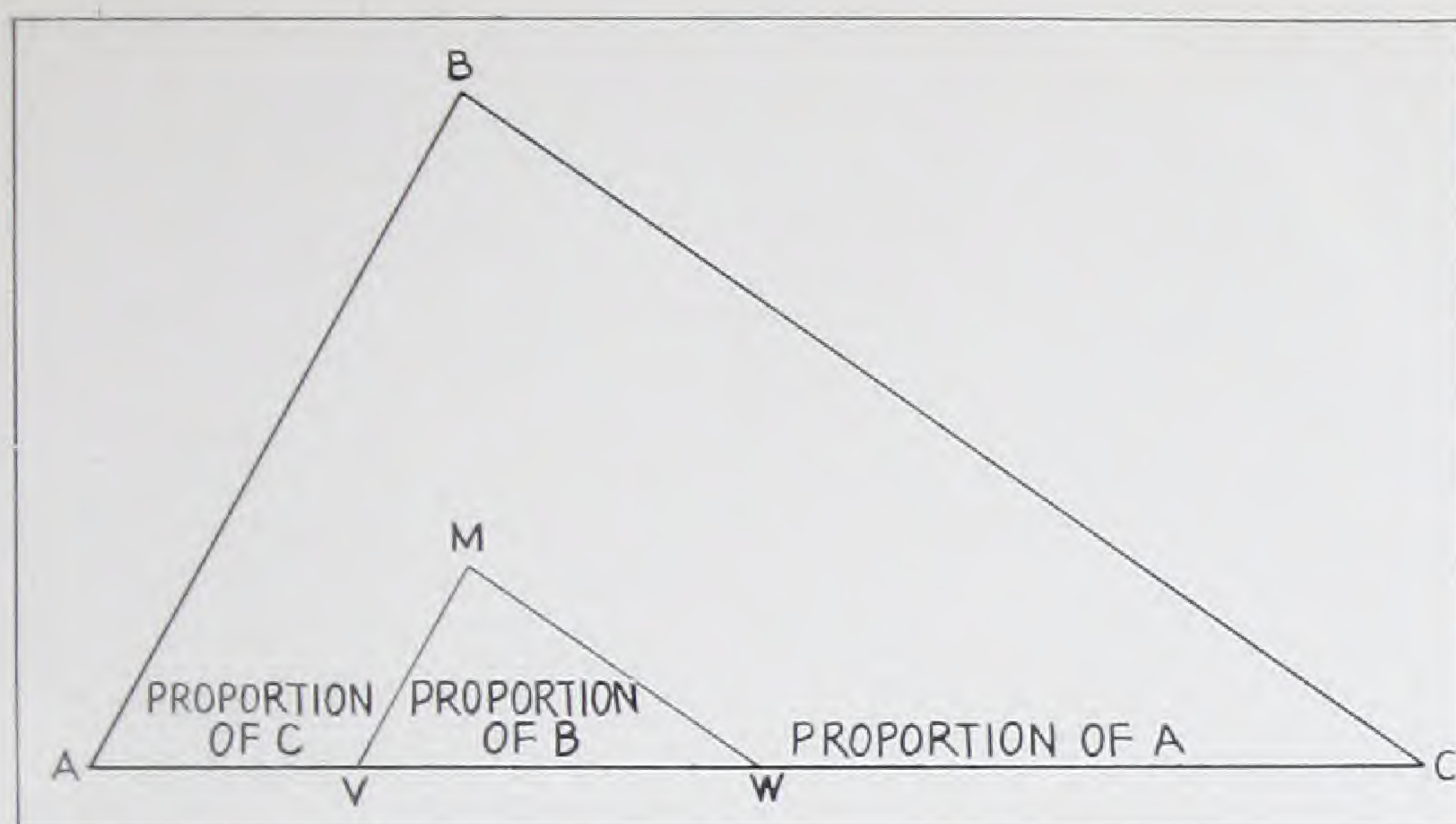


Fig. 2: Estimation of composition at a given point M

designate 10 percent intervals, or other suitable intervals, along the sides of the diagram, as shown along part of the base AC in Fig. 1. These points are represented by short segments of the longer lines in the figure.

Fig. 2 illustrates a method of estimating the composition at any given point within a triangular diagram, in this case point M, which is in the same location as in Fig. 1. Straight lines are drawn from M to one of the sides and parallel to the other two sides. Any side may be selected, but it is usually convenient to select the longest side, in this case the side AC. The lines MV and MW are parallel to the sides AB and BC, respectively. The intersections of these lines with AC divide the latter into three segments, and the lengths of these segments are relative proportions of A, B, and C in M. The intermediate segment VW is the relative proportion of B, the component at the opposite vertex. The segment for A is the one farthest from A, and the one for C is the one farthest from C. The procedure is reversed for locating any given composition in the diagram. Upon dividing the length of each segment by the length of the side AC, it is found that the composition of mixture M is 50 percent A, 30 percent B, 20 percent C.

The System $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$

The phase diagram of the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ is presented in Fig. 3. This diagram is essentially the same

as the original phase diagram of Rankin and Wright,¹ but with such modifications as were found necessary as a result of later investigations.^{3, 4, 5, 6} These modifications do not affect the portion of the system under study here, and will therefore not be discussed.

The phase diagram is a graphic representation of the data obtained in the investigation of the system. It not only reduces a large volume of data to a convenient form, but it also provides a base on which to operate in the interpretation of the data; that is, in applying the properties of the triangular diagram in the interpretation of the phase diagram, we are actually interpreting the data from which the phase diagram is obtained.

Each point in the phase diagram represents a state of equilibrium, or a state of rest. Since a process represents changes of some kind, not a state of rest, the phase diagram does not represent processes. It is useful, however, in studying processes, with the aid of additional information or assumptions. For example, the normal course of crystallization of a liquid in the system may be traced by assuming that at each temperature a state of equilibrium is attained before cooling to a slightly lower temperature. Each successive equilibrium state may be found from the phase diagram. The course of crystallization in an actual process may differ considerably from this if the assumption of continuous attainment of equilibrium does not apply to the process.

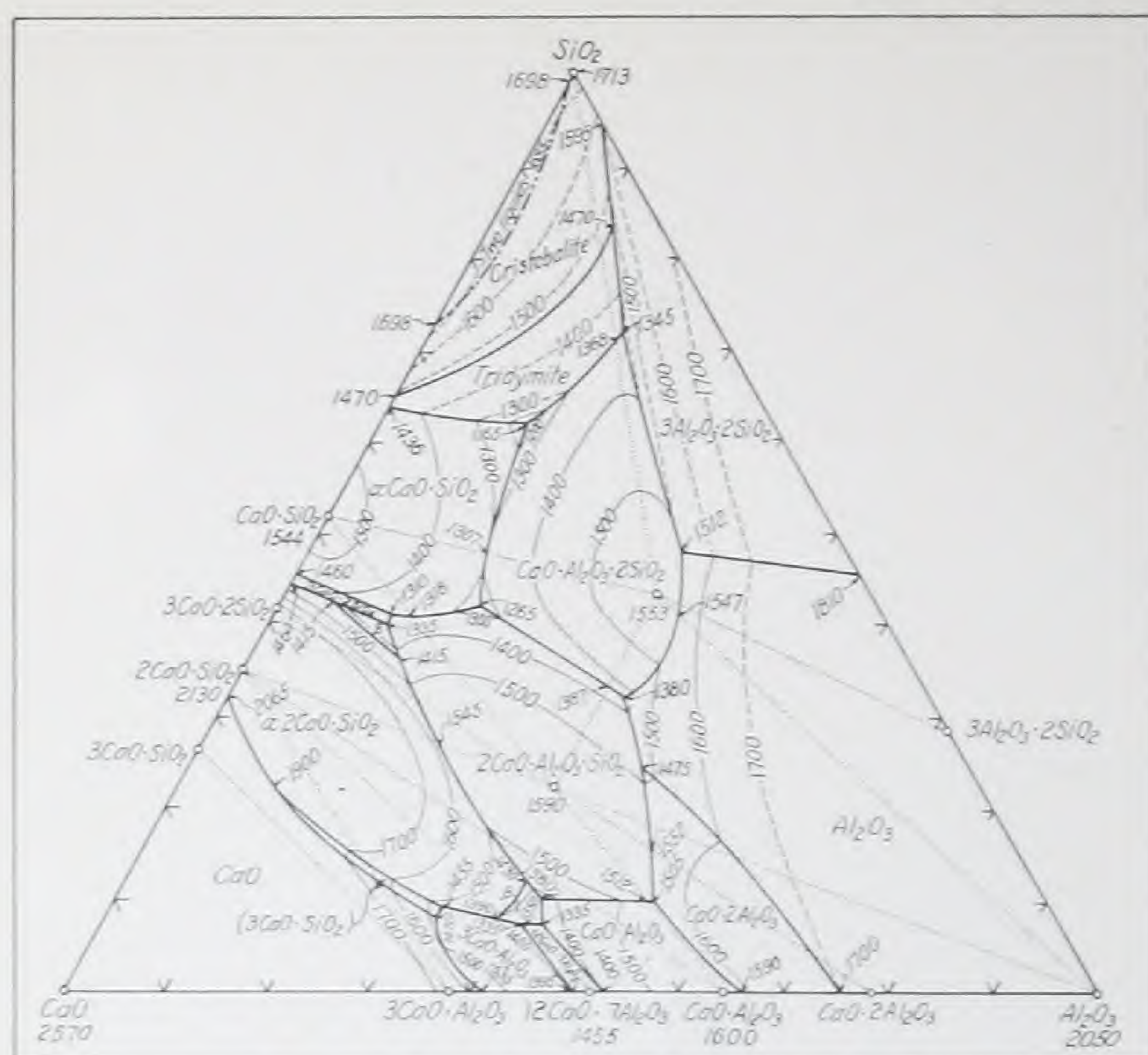


Fig. 3: Phase diagram of the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ (Rankin and Wright, as modified by later investigators)

When a pure crystalline compound is heated, it may decompose, or it may arrive at a definite temperature, or melting point, without decomposition. In the latter case it melts, without change of temperature, until it is completely transformed into a liquid of the same composition. Upon cooling, the liquid solidifies at the same temperature; that is, at the melting temperature. In a mixture such as those encountered in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ the situation is quite different. The mixture starts to melt at some definite temperature, and some crystalline phases are present as that temperature is maintained. The quantity of liquid increases as the temperature rises. Eventually a temperature is reached at which all of the crystalline substances are absent. This is sometimes termed the melting point. However, it is not a melting point in the same sense as in the case of the pure crystalline compound which melts without decomposition. The solid phase present at a temperature slightly below the complete fusion is not of the same composition as the liquid, but can exist in equilibrium with the liquid until the temperature is raised to complete the process of fusion. Because of this difference between the melting

point of a crystalline compound and the temperature at which a mixture becomes completely liquid, we prefer to term the latter the "temperature of complete fusion."

The significance of the various points, curves, and areas in the diagram may be understood by considering one of the methods of locating them. Let us suppose that we are starting out with no knowledge of phase relations in the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, which we propose to investigate. All that we have at the outset is the triangle, with CaO , Al_2O_3 , and SiO_2 designated at the vertices. Mixtures represented by points in the diagram are heated until completely liquified. Upon cooling, crystalline phases separate out. Usually only one crystalline phase separates out at first, and this is followed by the appearance of others as crystallization proceeds. The first one to appear is known as the primary phase. A particular crystalline phase may be the primary phase for liquids in one region of the diagram, while another crystalline phase may be characteristic of another region. The problem is to map out these "primary phase regions." A large number of compositions must be investigated to establish the boundaries

between the primary phase regions. In each region the primary phase must be identified. A common method is to heat each mixture until it is completely melted, then cool to a temperature slightly below the temperature of complete fusion. The mixture is then "quenched" — that is, cooled so suddenly that further crystallization does not occur. The mixture then consists of glass, in which the primary phase crystals are imbedded. The identity of the crystalline phase is determined by its optical properties, as observed microscopically.

In the course of locating boundaries between primary phase regions and identifying the primary phase in each, the temperature of complete fusion of each mixture is observed and recorded. At this stage the boundaries of the primary phase regions have been drawn in the diagram, the primary phase in each region has been indicated, and the observed temperatures have been used to locate isotherms, as in Fig. 3.* All of the experimental data are now shown in the diagram, but there are some further steps involved in completing Fig. 3, for convenience in the interpretation of the diagram. The composition of each crystalline phase is calculated from its chemical formula, and a point representing that composition is located in the diagram. For example, $3\text{CaO}\cdot\text{Al}_2\text{O}_3$, or tricalcium aluminate, is one of the primary phases. Its composition is 62.26 percent CaO, 37.74 percent Al_2O_3 , and it is located on the base at a point such that its distance from the CaO vertex is 0.3774 times the length of the base. Points representing the other primary phases are located in a similar manner.

Another addition to the diagram is the system of dotted lines separating the diagram into smaller triangles representing final products of crystallization. In the case of each triangle the crystalline phases at its vertices are the crystalline phases present in all compositions within the triangle when

crystallization is completed in a slow cooling operation. A definite plan is followed in determining which points representing primary phases should be connected by straight lines. If two primary phase regions are adjacent, a line is drawn between the points representing those phases. For example, the primary phase regions for $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ and Al_2O_3 adjoin. A line is therefore drawn between the points representing those phases.

The interpretation of the phase diagram is simplified by the assumption that the crystalline phases are pure compounds. According to Rankin and Wright,¹ solid solution "occurs only in the case of $\text{CaO}\cdot\text{SiO}_2$ and then only to the extent of 2 percent with each of the compounds with which it is associated; namely, SiO_2 , $3\text{CaO}\cdot 2\text{SiO}_2$, $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$, and $2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$." This does not involve the portion of the system in which we are interested. However, the fact that the boundary between the $\alpha\text{C}_2\text{S}$ region and one of the $\beta\text{C}_2\text{S}$ regions in Fig. 3 is clearly not an isotherm indicates that solid solution in the C_2S phase influences the α - β inversion temperature. This is also shown in Rankin and Wright's Table VI. The assumption that the crystalline phases are pure compounds is not strictly correct. However, the extent of impurity in the crystalline phases in the ternary system is not sufficient to necessitate taking it into account in the interpretation of the ternary phase diagram with reference to the manufacture of portland cement clinker. We shall, therefore, continue to treat the crystalline phases as pure compounds.

In describing a procedure by which the various regions in Fig. 3 may be mapped out, we emphasized that all liquids in any particular region are alike with reference to the first crystalline phase which appears upon cooling. That emphasis was necessary because we were describing a procedure in which the essential operation is determination of the first, or primary, phase. However, interpretation of the phase diagram involves a more precise concept of the significance of the re-

*All temperatures in this paper, both in figures and text, are expressed in degrees Centigrade.

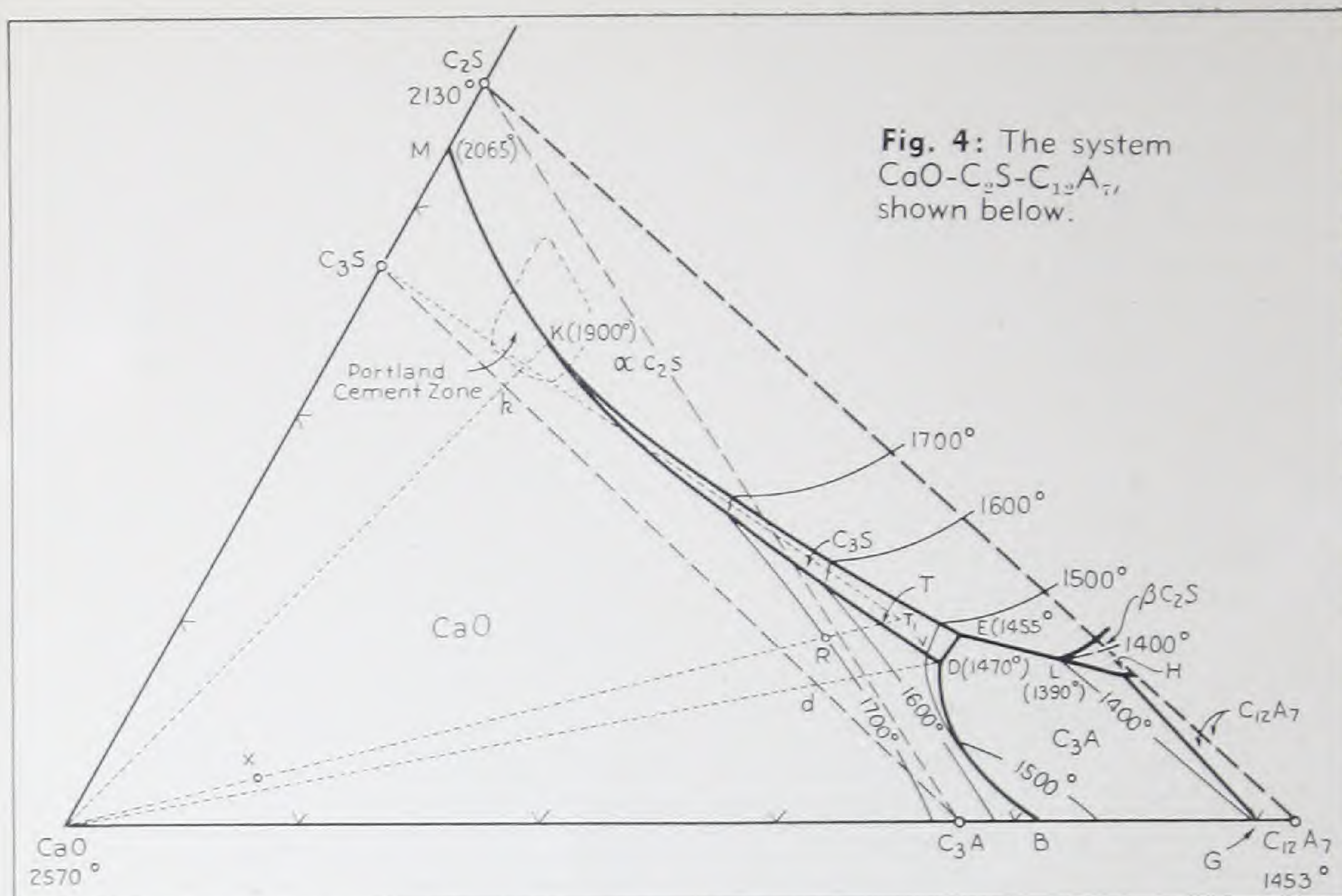


Fig. 4: The system $\text{CaO}-\text{C}_2\text{S}-\text{C}_{12}\text{A}_7$ shown below.

gions, their boundaries and intersections of the boundary curves. To illustrate, let us consider the CaO primary phase region in Fig. 4,* which is a portion of the phase diagram in Fig. 3. Liquid R on the 1700 deg. isotherm can exist by itself as a liquid at that temperature, or it may exist at equilibrium with any quantity of crystalline CaO at that temperature. That is, a mixture of liquid R and solid CaO may be maintained at that temperature indefinitely without the occur-

rence of any reaction. All mixtures of liquid R and solid CaO are on the dotted line CaO-R. Therefore, all mixtures on that line between CaO and R are composed of solid CaO and liquid R when equilibrium is attained at 1700 deg.

*In Fig. 4 abbreviated formulas are used for compounds of CaO, Al_2O_3 and SiO_2 . These oxides are designated as C, A, and S, respectively. Thus, $\text{C}_2\text{S} = 2\text{CaO} \cdot \text{SiO}_2$; $\text{C}_3\text{S} = 3\text{CaO} \cdot \text{SiO}_2$; $\text{C}_3\text{A} = 3\text{CaO} \cdot \text{Al}_2\text{O}_3$; and $\text{C}_{12}\text{A}_7 = 12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$. These abbreviated formulas will be used in the remainder of the paper.

Part II: The course of crystallization

TO ILLUSTRATE THE MANNER IN WHICH THE NORMAL COURSE OF CRYSTALLIZATION† of a liquid in the system may be traced, let us consider liquid X, which is on the line CaO-R. Judging from the position of X with reference to the isotherms and the melting point of CaO (2570 deg.), we would estimate the temperature of complete fusion of X to be about 2350 deg., and will assume that to be the case. Solid CaO appears when liquid X is cooled just below 2350 deg., and

†The normal course of crystallization refers to an ideal process, in which equilibrium is attained at each temperature before another small decrease in temperature occurs.

increases in amount as the temperature is lowered. As the quantity of solid CaO increases the liquid changes in composition in a direction away from the CaO vertex. At 1700 deg. the liquid is at point R. Since the line CaO-X is one-fourth of the line CaO-R, the mixture consists of 25 percent liquid R and 75 percent solid CaO at 1700 deg.

As the mixture cools below 1700 deg. the liquid continues to change in composition in a direction directly away from CaO until at about 1550 deg. it arrives at T, which is on the boundary between the CaO and C_3S

primary phase regions. It might seem that with a little further cooling the liquid would change in the same direction to a point inside the C_3S region, such as T_1 . However, the only solid phase with which a liquid in the C_3S region can exist in equilibrium is C_3S . Movement of the liquid to T_1 would involve a decided change from a state in which the phases are solid CaO and liquid to one in which they are solid C_3S and liquid. The matter may be tested by drawing the line C_3S-T_1 . Since X is not on the line C_3S-T_1 , this is an impossible condition if equilibrium is to be continuously attained. On the other hand, the liquid might change in composition along the curve TD , and this possibility can be tested. Since V is on the boundary between the CaO and C_3S primary phase regions, and also on the 1500 deg. isotherm, liquid V may exist in equilibrium with CaO and C_3S at that temperature. Without drawing the necessary lines, it is readily seen that X is in the triangle $C_3S-V-CaO$. It is therefore known that the liquid follows the curve TV and, by the same procedure, that it follows the curve beyond V to D .

The primary phase regions for CaO , C_3S and C_3A meet at point D . At 1470 deg., liquid D is capable of existing in equilibrium with these three solid phases. CaO and C_3S are the solid phases present when the liquid arrives at D , but C_3A appears and crystallization proceeds with liquid D present, so that there are now four phases present, liquid D and solid CaO , C_3S and C_3A . The process continues without change of temperature until one of these phases disappears. There are four combinations of three phases each, as follows:

1. CaO , C_3S , liquid D
2. CaO , C_3A , liquid D
3. C_3S , C_3A , liquid D
4. CaO , C_3S , C_3A

The first combination represents the phases present when the liquid arrived at D . Mixture X cannot be formed from the phases in combinations 2

and 3, since X is not in the triangle formed by joining the points indicated in either combination. Combination 4 is possible, since X is in the triangle $CaO-C_3S-C_3A$. In this way it is found that crystallization of mixture X proceeds to completion with the liquid path ending at D . A study of the course of crystallization of other mixtures in triangle $CaO-C_3S-C_3A$ leads to division of the triangle into three areas which differ in the order of appearance and disappearance of solid phases in the normal course of crystallization. In each area, normal crystallization begins with the appearance of the primary phase, CaO , and ends with liquid D present until the last drop of liquid disappears. The three areas, with the solid phases listed in the order in which they are present, are indicated below.

1. Triangle $CaO-C_3S-k$.
 CaO ; CaO , C_2S ; CaO , C_3S , C_2S (at point K); CaO , C_3S ; CaO , C_3S , C_3A .
2. Triangle $CaO-k-d$.
 CaO ; CaO , C_3S ; CaO , C_3S , C_3A .
3. Triangle $CaO-d-C_3A$.
 CaO ; CaO , C_3A ; CaO , C_3S , C_3A .

The reason for the plan which was followed in choosing the pairs of compounds which are joined by the dotted lines in Fig. 3, may now be understood. For each triangle so obtained there is a corresponding point at which three primary phase regions meet, and these primary phases are those at the vertices of the triangle. At this point crystallization of all compositions in the triangle are completed. For example, liquids in the triangle $C_3S-C_2S-C_3A$ normally complete their crystallization with the liquid at point E , Fig. 4, until the last drop of liquid disappears, leaving only solid C_3S , C_2S and C_3A . Point E is outside of the triangle $C_3S-C_2S-C_3A$, and is therefore classed as a peritectic point. Point D is also a peritectic point. A point inside the triangle which defines the range of compositions that complete their crystallization at the point is classed as a

eutectic point. Both eutectic and peritectic points are invariant points.

When the liquid phase is at an invariant point, changes in proportions of phases occur without change in temperature. This was shown in the crystallization of composition X, Fig. 4. When the liquid arrived at D, three phases were present, solid CaO, C_3S , and liquid D. Another phase, solid C_3A , appeared, and there were then four phases present. The proportions of these phases changed until finally one phase, liquid D, disappeared. These changes in proportions of phases which occur at a constant temperature involve changes in heat content. During crystallization, or the reverse process of fusion, at an invariant point there is a tendency to maintain a constant temperature until the changes in phase composition are completed. This appears in the curve obtained when temperature during cooling or heating is plotted against time. When the difference between maximum and minimum heat content at a particular temperature is large, there may be a step in the curve. Significant points at which energy changes occur are not always readily seen on the time-temperature curve, particularly when small quantities of materials are used in a test. These points are sometimes found by a method of magnifying the effect of an energy change, known as differential thermal analysis. This method is useful in locating invariant points and other points of energy change.

The System C_3S - C_2S - C_3A

The raw materials used in the manufacture of portland cement clinker contain Fe_2O_3 , MgO and a number of minor constituents in addition to the three oxides, CaO , Al_2O_3 and SiO_2 . However, it is possible to make portland cement clinker containing only the three oxides, on a laboratory scale. Such clinkers are located in the triangle C_3S - C_2S - C_3A , (Fig. 3). The approximate range of compositions of the three oxides comparable with the commercial product is designated as the "portland cement zone" in Fig. 4.

Invariant points in the system CaO - C_2S - $C_{12}A_7$ are listed below:

Point	Temp. (Cent.)		CaO	Al_2O_3	SiO_2
M	2065	CaO , αC_2S	67.5	—	32.5
B	1535	CaO , C_3A	57.0	43.0	—
G	1395	C_3A , $C_{12}A_7$	50.0	50.0	—
K	1900	CaO , αC_2S , C_3S	68.4	9.2	22.4
L	1390	αC_2S , βC_2S , C_3A	54.5	38.0	7.5
H	1335	βC_2S , C_3A , $C_{12}A_7$	52.0	41.2	6.8
D	1470	CaO , C_3S , C_3A	59.7	32.8	7.5
E	1455	C_3S , C_2S , C_3A	58.3	33.0	8.7

The final products of crystallization of liquids or partially fused materials in the triangle C_3S - C_2S - C_3A are the compounds at the vertices of the triangle. In studying the changes which occur in the clinkering process, it is convenient to transform oxide compositions to composition expressed in terms of these compounds. The compound compositions may be calculated for mixtures of the three oxides which have not actually been combined to form the compounds. The calculated compound composition may be termed the *potential* composition, to avoid the implication that the compounds are necessarily present in the calculated proportions. In any case, however, the potential composition indicates the percentages of the compounds which would be present if the oxides were combined to form the three compounds. The potential composition may be calculated from the oxide composition by substitution in the following equations, in which the coefficients are based upon 1952 atomic weights.

$$\begin{aligned} C_3S &= 4.0715 CaO - 7.5996 SiO_2 - 6.7182 Al_2O_3 \quad (1) \\ C_2S &= 8.5996 SiO_2 + 5.0681 Al_2O_3 - 3.0715 CaO \quad (2) \\ \text{or, } C_2S &= 2.8665 SiO_2 - 0.7544 C_3S \quad (2a) \\ C_3A &= 2.6501 Al_2O_3 \quad (3) \end{aligned}$$

In these equations the chemical formulas refer to percentages of the indicated compounds or oxides. For example, equation 3 may be expressed:

$$\% C_3A = 2.6501 (\% Al_2O_3)$$

The potential compositions of mixtures in the system C_3S - C_2S - C_3A are shown graphically in Fig. 5. The triangle C_3S - C_2S - C_3A is divided into 10 percent intervals of each of the compounds, as described in connection with Fig. 1.

The line C_3S - C_3A is designated as the "theoretical lime limit." All compositions on this line contain sufficient

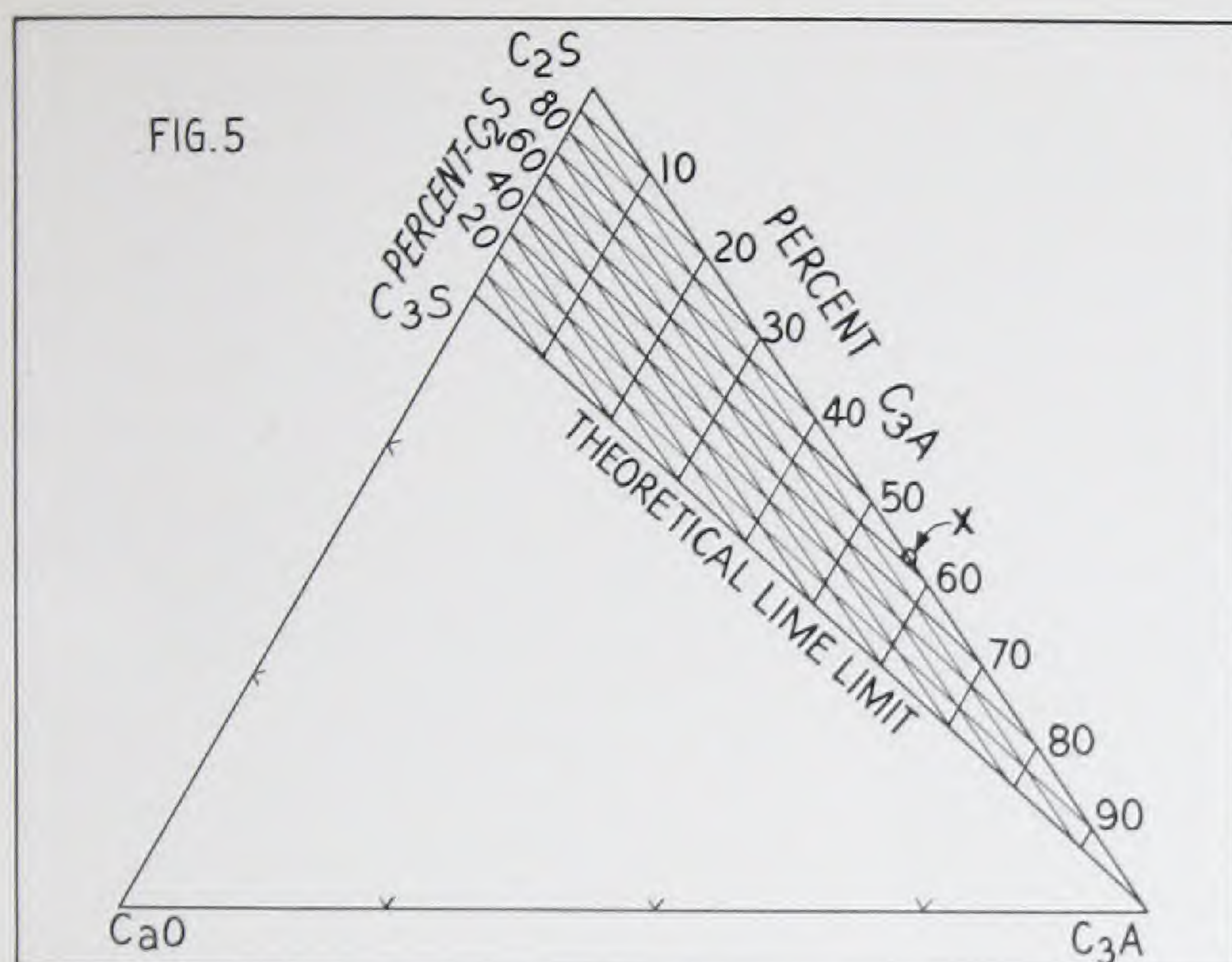


Fig. 5: Final products of crystallization in the system C_3S - C_2S - C_3A

CaO to convert all of the SiO_2 present to C_3S and all of the Al_2O_3 present to C_3A . Any excess of CaO beyond that amount of CaO must be uncombined. This is in addition to any free lime which may be present because of poor burning or other reasons. The line representing the theoretical lime limit also represents zero percent potential C_2S . Thus, the theoretical lime limit is attained when the potential C_2S is zero, or when

$$CaO = 2.80 SiO_2 + 1.65 Al_2O_3.$$

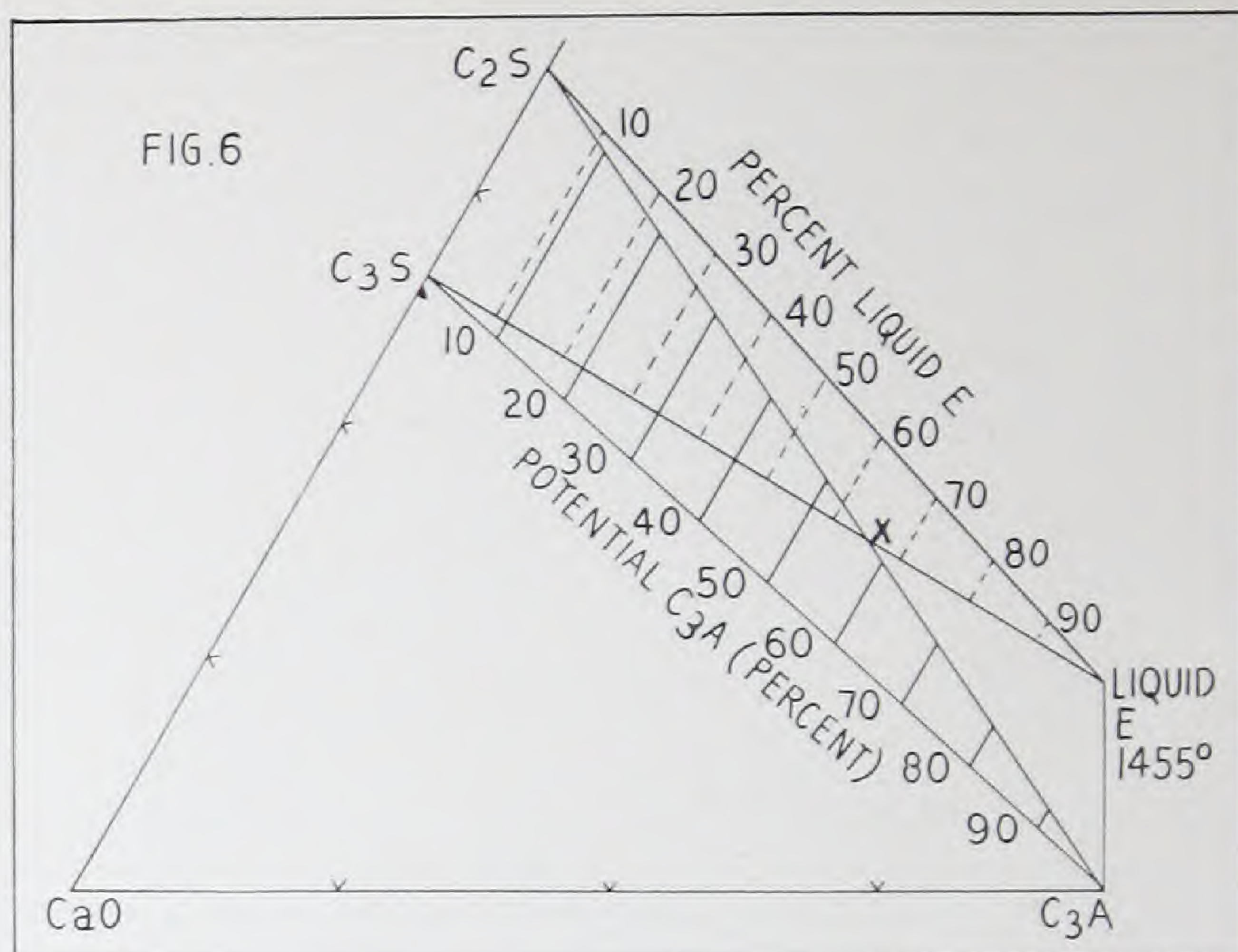
Point X on the line $C_2S - C_3A$ represents the composition 41.9 percent C_2S , 58.1 percent C_3A . That is the composition when crystalline equilibrium is attained at 1455 deg. It will be shown presently that this mixture has a quite different phase composition when the heat content is maximum at that temperature.

When a mixture in the system C_3S - C_2S - C_3A is maintained at 1455 deg., liquid E and the solid phases C_3S , C_2S and C_3A may coexist in a state of equilibrium. However, as heat is added to the system at 1455 deg., the maximum heat content and maximum quantity of liquid E are attained simultaneously, and one of the solid phases disappears. The proportions of solid phases and liquid may be estimated by joining point E, Fig. 4, with the points representing the solid

phases. This is shown in Fig. 6 for the case in which solid C_3A disappears, leaving C_3S , C_2S and liquid E. The triangles C_3S - C_2S - C_3A and C_3S - C_2S -E have a common base, and the lines representing potential C_3A in one and percent liquid in the other, are consequently parallel. It is apparent that for cement compositions in the triangle C_3S - C_2S -X the percent liquid E is proportional to the potential C_3A .

Considering the position of point X on the line C_3S -E, and the lengths of the segments C_3S -X and XE, it is seen that at 1455 deg., maximum heat content, a mixture of that composition is composed of 33.5 percent C_3S , 66.5 percent liquid E. If the mixture is quenched while in that state, so that the liquid is frozen to a glass, the cooled material will contain 33.5 percent C_3S , 66.5 percent glass. On the other hand, if it is cooled slowly, so that normal crystallization occurs, it will contain 41.9 percent C_2S , 58.1 percent C_3A , and no C_3S . As mentioned previously in discussing Fig. 5, the appearance of C_3S in greater quantity than in the crystallized product applies to all compositions in the system C_3S - C_2S - C_3A , but the effect is greatest at point X. It is due to the fact that invariant point E is outside of the system, in a direction away from the C_3S vertex. If point E were inside the

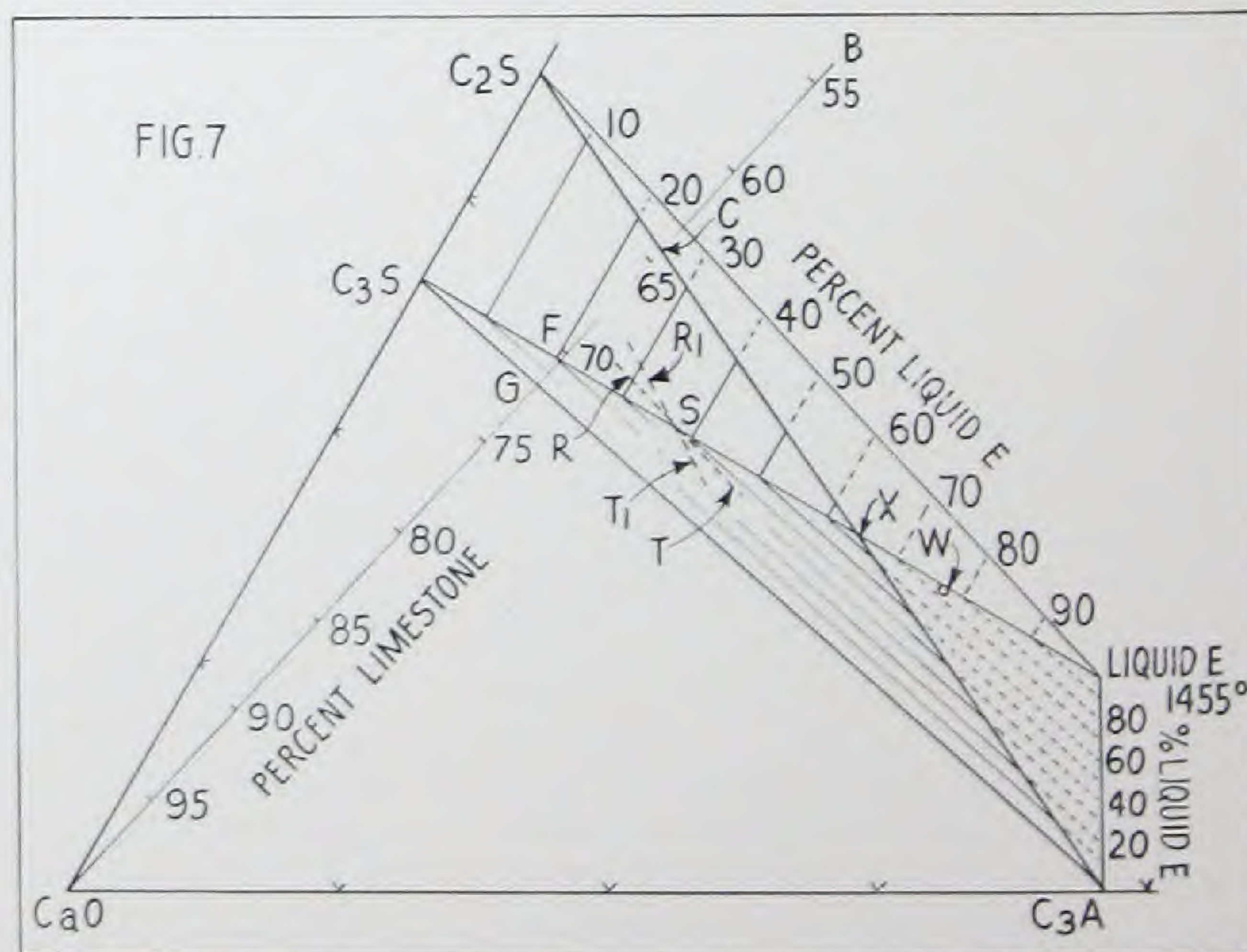
Fig. 6: Percent liquid at 1455 deg.
(max. heat content) for compositions in the triangle C_3S - C_2S - x



triangle C_3S - C_2S - C_3A , this effect would not appear. The increase in the percentage of C_3S through quenching at the temperature of liquid formation may seem to offer promise as a method of manufacturing a high early strength cement (high C_3S). However, the condition applies to portland cements made from the three oxides, and does not apply when other oxides, such as Fe_2O_3 , or Fe_2O_3 and MgO , are added to the system. It serves to illustrate the fact that burning and cooling conditions play an important part in determining the chemical nature of the final product.

In Fig. 7 the proportions of liquid at 1455 deg., maximum heat content, are shown for the entire system C_3S - C_2S - C_3A . In the discussion of Fig. 6 it was shown that, for compositions in the triangle C_3S - C_2S - X , solid C_3A disappears when the quantity of liquid reaches a maximum at 1455 deg., and the percent of liquid is proportional to the *potential* C_3A . A similar situation exists in the triangle C_3S - X - C_3A . Here C_2S disappears when the quantity of liquid reaches a maximum at 1455 deg., and the percent of liquid is proportional to the *potential* C_2S . That the latter is true may be readily

Fig. 7: Percent liquid at 1455 deg.
(max. heat content)



seen. Lines representing 10 percent intervals of potential C_2S are parallel to the C_3S - C_3A side of the triangle, as shown in Fig. 5. The lines representing 10 percent intervals of liquid in the triangle C_3S - X - C_3A are also parallel to that side, so that the percent of liquid is proportional to the potential C_2S .

The percent of liquid in a mixture in the system C_3S - C_2S - C_3A , at maximum heat content at 1455 deg., may be estimated from Fig. 7 by locating the composition in the diagram. The quantity of liquid may be increased by raising the temperature. This will be considered presently. However, it is of interest to consider the relation of composition to liquid content at 1455 deg. (the lowest clinkering temperature) in a manner more closely related to control of composition in the manufacturing process. The raw materials commonly used in the manufacture of portland cement clinker are limestone and clay or shale. For a comparable situation in the ternary system, we will let pure CaO represent limestone and a mixture composed of 77 percent SiO_2 , 23 percent Al_2O_3 represent clay. The line CaO - B in Fig. 7, when extended, passes to the point representing the clay. These materials will be referred to as limestone and clay, to carry out the comparison with the commercial process. It will be assumed that the materials are pulverized. Proportions of the two materials will be expressed on an ignited weight basis.

Starting at 55 percent limestone and passing toward the CaO vertex, the C_3S - C_2S - C_3A triangle is encountered at point C (64.5 percent limestone). At this point, 25 percent liquid E is present at maximum heat content, sufficient to cause the agglomeration of particles into a clinker. As the percent of limestone is increased, the proportion of liquid is reduced, until at F , (70.5 percent limestone) about 20 percent liquid E is present. Throughout this range, the quantity of liquid is sufficient to act as a medium through which chemical reaction can occur

toward the attainment of equilibrium; that is, the temperature of liquid formation, 1455 deg., is sufficient for the accomplishment of the desired reactions, and there is no need of raising the temperature.

In the region between C and F the effect of changes in percentage of limestone on liquid content is not great, since the lines representing 10 percent intervals in liquid content are far apart, and the line CaO - B makes only a small angle with them. After passing the line C_3S - E at F , the percent of liquid is governed by the potential C_2S , as shown previously. In this region the lines representing 10 percent intervals of liquid E are closely spaced, and they are crossed almost at right angles by the line CaO - B . The small increase of 1.2 percent in the proportion of limestone in passing from F to G is accompanied by a decrease in liquid content from about 20 percent to zero. Higher temperatures are required to secure sufficient liquid, but in this range of compositions the increase in liquid content may be accompanied by other undesirable conditions which will be discussed presently.

One of the most important considerations is controlling proportions of materials in the manufacture of cement clinker is that of securing a liquid content which will lead to the attainment of equilibrium in a reasonable time. From the foregoing study of Fig. 7 with reference to conditions at the temperature of liquid formation, it may be readily understood that for ternary compositions between C and F the control of proportions of limestone and clay is not nearly as critical as in compositions between F and G . In fact, the effect of a change of 1.00 percent in the percentage of limestone on the percent of liquid E is 24 times as great between F and G as it is between C and F .

It has been found in the foregoing study that in the case of mixtures in the triangle C_3S - X - C_2S , the quantity of liquid at 1455 deg. is proportional

to the potential C_3A , while in the triangle C_3S - X - C_3A the quantity of liquid E is proportional to the potential C_2S . This has been demonstrated graphically. A similar situation exists when other components are added to the system, as in the case of commercial portland cement clinker. To demonstrate this similarity it will be nec-

essary to compute percentages of solid phases and liquids, since graphic methods such as those which have been used for the ternary system are not adequate when the number of components is increased. The method of computing phase composition, that is, composition expressed in terms of the phases present, will now be described.

Part III: Computation of phase composition

TO ILLUSTRATE THE PROCEDURE in computation of phase composition, let us consider the problem of calculating the weight fraction of liquid E in a mixture of the composition 70.15 percent CaO , 8.30 percent Al_2O_3 , 21.55 percent SiO_2 . Liquid E , which is capable of existing in equilibrium with solid C_3S , C_2S and C_3A at 1455 deg., has the composition 58.3 percent CaO , 33.0 percent Al_2O_3 , 8.7 percent SiO_2 . As this liquid is formed it withdraws CaO , Al_2O_3 and SiO_2 from the solid portion of the mixture in the proportions required for its formation, as indicated in the composition of the liquid. Let m represent the weight fraction of liquid at any given time. Then in 100 grams of mixture, the components in the solid residue are as follows:

$$\text{Grams } CaO = 70.15 - 58.3m \quad (4)$$

$$\text{Grams } Al_2O_3 = 8.30 - 33.0m \quad (5)$$

$$\text{Grams } SiO_2 = 21.55 - 8.7m \quad (6)$$

For any value of m , from zero to a certain maximum, the equations will give the percentages of CaO , Al_2O_3 and SiO_2 in the solid residue, expressed in terms of the mixture as a whole. The maximum value of m remains to be determined. It is apparent that m cannot exceed $8.30/33.0$, or 0.2515, since the Al_2O_3 in the residue is then zero, and no Al_2O_3 remains for continuing the formation of liquid. However, this method of determining the maximum value of m assumes that any residue which remains is capable of existing in equilibrium with liquid E . This assumption is not sound. The residue must consist only of solid phases capable of existing in

equilibrium with liquid E ; that is, one or more of the phases C_3S , C_2S and C_3A . To obtain a value of m which will leave such a residue, the compositions of both liquid E and the mixture may be expressed in terms of C_3S , C_2S and C_3A . The potential compound composition of each may be computed by substitution in equations 1-3, obtaining the compositions indicated below:

	Mixture	Liquid E
C_3S	66.1%	-50.4%
C_2S	11.9	63.0
C_3A	22.0	87.4
	<hr/> 100.0%	<hr/> 100.0%

The potential C_3S in liquid E is negative because liquid E is outside of triangle C_3S - C_2S - C_3A in a direction away from the C_3S vertex, as shown in Fig. 4. The potential compositions are used in setting up equations similar to equations 4-6, as follows:

$$\text{Solid } C_3S = 66.1 + 50.4m \quad (7)$$

$$\text{Solid } C_2S = 11.9 - 63.0m \quad (8)$$

$$\text{Solid } C_3A = 22.0 - 87.4m \quad (9)$$

The value of m is the smallest value which will reduce one of the equations to zero. From equation 8, $m = 11.9/63.0$, or 0.1889. From equation 9, $m = 22.0/87.4$, or 0.2517. The smaller of these values, 0.1889, is the maximum value of m to be applied in equations 4-6 or 7-9. Substituting in equations 7-9, we obtain the following:

$$\begin{array}{rcl} \text{Solid } C_3S & = & 66.1 + 50.4 \times 0.1889 = 75.62\% \\ \text{Solid } C_2S & = & 11.9 - 63.0 \times 0.1889 = 0.00 \\ \text{Solid } C_3A & = & 22.0 - 87.4 \times 0.1889 = 5.49 \\ \text{Liquid } E & = & 100 \times 0.1889 = 18.89 \\ & & \hline & & 100.00\% \end{array}$$

The percentages of phases obtained by the foregoing method is in harmony with the required conditions, that the amount of liquid attains a maximum through the disappearance of one of the solid phases, and that the residue is composed of phases capable of existing in equilibrium with the liquid.

Comparison with the Quaternary System $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3$

The quaternary system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3$ has been investigated with reference to portland cement technology by Lea and Parker^{7,8} and by Swayze.⁹ Lea and Parker investigated

be used to avoid such difficulties. The system within the quaternary system which corresponds to the system $\text{C}_3\text{S-C}_2\text{S-C}_3\text{A}$ in the ternary system is the system $\text{C}_3\text{S-C}_2\text{S-C}_3\text{A-C}_4\text{AF}$. Portland cement clinker may be made from mixtures in either system, but those in the quaternary system may be burned at a lower temperature, and resemble commercial clinker more closely because of the presence of Fe_2O_3 , which is a constituent of all commercial cements. The potential composition of mixtures in the system $\text{C}_3\text{S-C}_2\text{S-C}_3\text{A-C}_4\text{AF}$ may be calculated by substitution in the following equations:

$$\text{C}_3\text{S}=4.0715 \text{ CaO}-7.5996 \text{ SiO}_2-1.4297 \text{ Fe}_2\text{O}_3-6.7182 \text{ Al}_2\text{O}_3 \quad (10)$$

$$\text{C}_2\text{S}=8.5996 \text{ SiO}_2+1.0786 \text{ Fe}_2\text{O}_3+5.0682 \text{ Al}_2\text{O}_3-3.0715 \text{ CaO} \quad (11)$$

or

$$\text{C}_2\text{S}=2.8665 \text{ SiO}_2-0.7544 \text{ C}_3\text{S} \quad (11a)$$

$$\text{C}_3\text{A}=2.6501 \text{ Al}_2\text{O}_3-1.6919 \text{ Fe}_2\text{O}_3 \quad (12)$$

$$\text{C}_4\text{AF}=3.0431 \text{ Fe}_2\text{O}_3 \quad (13)$$

the system $\text{CaO-C}_2\text{S-C}_3\text{A-C}_4\text{AF}$. The compound $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$, designated here as C_4AF , had been reported earlier by Hansen, Brownmiller and Bogue¹⁰ as the ferric oxide compound in portland cement, and was therefore selected as one of the components of the system to be investigated. In his investigation of the ternary system $\text{CaO-C}_3\text{A-C}_2\text{F}$, Swayze discovered the existence of a complete series of solid solutions from C_2F to a new compound, $\text{C}_6\text{A}_2\text{F}$. The composition C_4AF is in this series. In order to include the entire solid solution series in the quaternary system under investigation, it was necessary to investigate the system $\text{CaO-C}_2\text{S-C}_3\text{A-C}_2\text{F}$, which includes a wider range than the system investigated by Lea and Parker. Since some of the data required for mathematical treatment are lacking in Swayze's investigation, we will base our studies here on Lea and Parker's data.

A space model in the form of a tetrahedron is required for representation of a quaternary system. It will not introduce complexities in this study, since the method of computation which has been described will

With the exception of terms involving Fe_2O_3 , equations 10-12 are identical with equations 1-3.

The point in Lea and Parker's quaternary system corresponding to point E, Fig. 4, in the ternary system is designated as invariant point T_2 . The liquid at this point is capable of existing in equilibrium with solid C_3S , C_2S , C_3A and C_4AF at 1338 deg. The oxide composition and the potential compound composition of liquid T_2 are given below, the latter computed by substitution in equations 10-13.

Composition of liquid T_2

Oxides		Compounds	
SiO_2	6.0%	C_3S	1.4%
Al_2O_3	22.7	C_2S	16.2
Fe_2O_3	16.5	C_3A	32.2
CaO	54.8	C_4AF	50.2

In the ternary system we found that the potential C_3S at point E is negative, indicating that the point is outside of the triangle $\text{C}_3\text{S-C}_2\text{S-C}_3\text{A}$ in a direction away from the C_3S vertex. It was this condition that led to the presence of larger quantities of solid C_3S when liquid E is present than when crystallization is complete. The situation is not the same in the qua-

ternary system. At point T_2 the potential percentages of the compounds are all positive. The potential C_3S is a small positive value, indicating that point T_2 is barely inside the tetrahedron $C_3S-C_2S-C_3A-C_4AF$. Lea and Parker express some doubt as to whether the point is inside the tetrahedron (a eutectic) or outside (a peritectic), since small changes in the composition of the point, within the experimental error of determination, could place it on either side of the face of the tetrahedron. For our purpose it will be assumed that the reported composition is not subject to any error of this kind.

As an example of the computation of phase composition, we will consider the problem of calculating the percentages of solid phases and liquid T_2 in a mixture having the potential composition 44.8 percent C_3S , 35.6 percent C_2S , 7.0 percent C_3A , 12.6 percent C_4AF . Equations for the percentages of solid phases may be set up in the same manner as equations 7-9, with m representing the weight fraction of liquid T_2 , as follows:

$$\text{Solid } C_3S = 44.8 - 1.4m \quad (14)$$

$$\text{Solid } C_2S = 35.6 - 16.2m \quad (15)$$

$$\text{Solid } C_3A = 7.0 - 32.2m \quad (16)$$

$$\text{Solid } C_4AF = 12.6 - 50.2m \quad (17)$$

Equating each of the right-hand members to zero, and solving for m , it is found that equation 16 gives the lowest value of m , that is, $7.0/32.2$, or 0.217. Substituting in the equations, we find that

Solid C_3S	=	44.5%
Solid C_2S	=	32.1
Solid C_3A	=	0.0
Solid C_4AF	=	1.7
Liquid T_2	=	21.7
		100.0%

Equations 14-17 refer to one particular mixture in the system, for which the C_3A equation gave the lowest value of m , indicating that the potential C_3A determines the percent of liquid T_2 . In view of the complete range of compositions of mixtures in the system it may be readily under-

stood that in one range of compositions the potential C_3A determines the percent of liquid, in another the potential C_2S is the governing factor, etc. The four regions correspond to the areas C_3S-C_2S-X and C_3S-C_3A-X , Fig. 7, in which the percent liquid is determined by the potential C_3A or C_2S , respectively. In the space model of the quaternary system these regions are separated by planes meeting at the point T_2 .

In the cement industry the compounds C_3A and C_4AF are frequently referred to as "fluxes." The Al_2O_3 and Fe_2O_3 which enter into the formation of these compounds are present in the raw materials from which portland cement clinker is made, and are not commonly added to the raw mix to serve as fluxes. However, since they play a part in promoting fusion, they may be regarded as fluxes to the extent that they serve that purpose. Since it has been found that the percent of liquid is governed by the potential percentage of the compound which disappears when the liquid is formed, it is preferable to refer to the compounds, rather than the oxides, as fluxes. When the potential percentage of a particular compound determines the percent of liquid, the compound may be regarded as a flux, since it promotes fusion. However, the effect of increasing the quantity of that compound on the degree of fusion does not continue indefinitely. For example, consider a mixture at point R, Fig. 7, which is in the region in which the potential C_3A governs the percentage of liquid E. The dotted line RT is in a direction directly toward the C_3A point, and represents increasing potential C_3A . When the potential C_3A is increased to a point beyond S, such as T, the mixture is no longer in the region in which the potential C_3A governs the percentage of liquid. Point T is in the region in which the potential C_2S governs the percentage of liquid. The quantity of liquid is lowered in passing from S to T, but can be increased by increasing the potential C_2S . In considering fusion at

1455 deg. when the liquid phase is at E, C_3A is the flux in one region and C_2S in the other. Similarly, in the quaternary system, C_2S , C_3A or C_4AF may be regarded as a flux in the process of fusion at 1338 deg. when the liquid phase is at T_2 . Each of these compounds has a particular field of influence on the degree of fusion. The compound C_3S is ignored here because the potential C_3S at invariant point T_2 is so small that it is uncertain whether the point is eutectic or peritectic. In either case, it is negligible in dealing with portland cement compositions.

As in the ternary system, the quantity of liquid is proportional to the potential C_2S in low C_2S compositions at the temperature of liquid formation. This is in line with experience in the commercial process, that low C_2S compositions are difficult materials to burn.

Changes in composition may play a part in the sloughing off of clinker coating or the development of rings in the hot zone of the kiln. The line R_1T_1 in Fig. 7 has been introduced to illustrate the condition. The line is drawn at an angle of 60 deg. with the base $CaO-C_3A$, so that all compositions on the line are identical in CaO content. The SiO_2/Al_2O_3 ratio increases in passing from T_1 to R_1 . The liquid content increases in passing from R_1 to S, and then decreases in passing on to T_1 . Let us suppose that composition R_1 is maintained in the kiln, and that a coating of that composition has been built up. If the SiO_2/Al_2O_3 ratio in the clay or shale drops, so that the clinker has the composition T_1 , there is opportunity for development of a greater liquid content, such as S, at the contact between clinker and coating. This may lead to sloughing off clinker coating in some instances, or building up clinker coating in others, depending upon the general level of compositions maintained. The effect of an abrupt change in SiO_2/Al_2O_3 ratio is the same whether the ratio increases or decreases. The possibility of its occurrence depends upon the basis for composition con-

trol. For example, with a constant CaO content, as on the line R_1T_1 , a change in SiO_2/Al_2O_3 ratio may cause the liquid content to rise to a maximum, as at S, and then to fall. With a constant potential C_2S the liquid content may rise to a maximum as the SiO_2/Al_2O_3 ratio decreases, and the liquid content then remains constant, not falling, with further decrease in the ratio. The choice of basis for composition control may be important in avoiding some abnormalities in retention of clinker coating.

Equilibria above the Temperature of Liquid Formation

So far we have considered equilibria at the temperature of liquid formation, which is 1455 deg. in the ternary system $C_3S-C_2S-C_3A$, and 1338 deg. in the quaternary system $C_3S-C_2S-C_3A-C_4AF$. Higher temperatures may be employed to increase the quantity of liquid, to accelerate the chemical reactions involved in the production of portland cement clinker. States of equilibrium in the ternary system at higher temperatures will now be considered.

It has been shown in the study of Fig. 7 that at maximum heat content at 1455 deg. the phases in mixtures in triangles C_3S-C_2S-E and C_3S-C_3A-E are those indicated at the vertices. With further heating the temperature rises, and the liquid follows a boundary curve. It should be noted that E (Fig. 4) is at the intersection of three boundary curves, and can be considered as being on each one of the three curves. The solid phases present when the heat content is at a maximum at 1455 deg. indicates the boundary curve which will be followed when the temperature is raised. For example, a mixture in the triangle C_3S-C_2S-X consists of solid phases C_3S , C_2S and liquid E at 1455 deg. maximum heat content. As the temperature is raised, the liquid follows the boundary between the C_3S and C_2S primary phase regions, starting at E (Fig. 4). Similarly, when the temperature of a mixture in the triangle C_3S-C_3A-X is

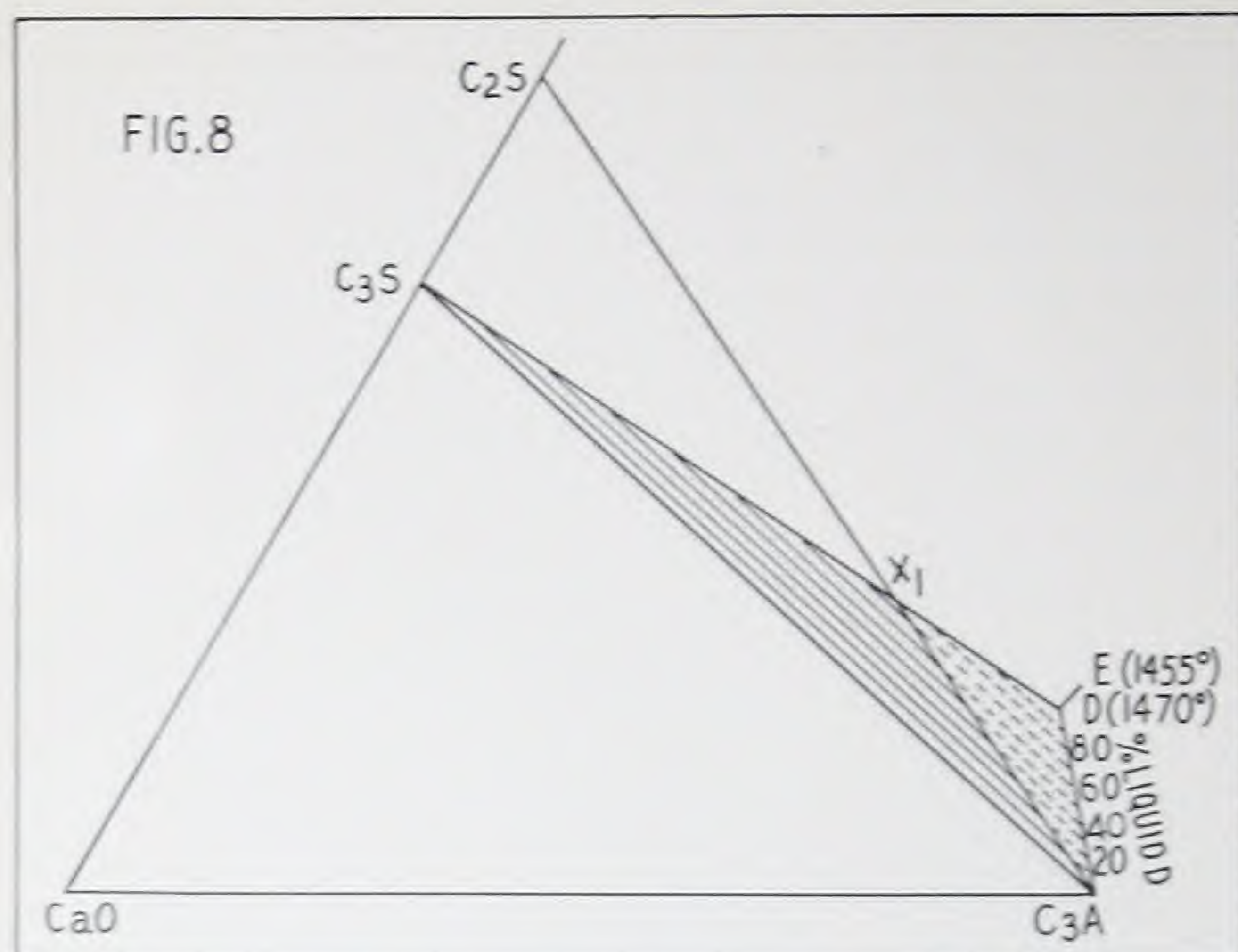


Fig. 8: Percent liquid at 1470 deg. (min. heat content)

raised above 1455 deg. the liquid follows the boundary between the C_3S and C_3A primary phase regions.

Referring to Fig. 4, it is seen that the boundary between the C_3S and C_2S primary phase regions passes from E almost directly toward the C_3S point. Point W in Fig. 7 is on this boundary, near the 1600 deg. isotherm. As mixtures in the triangle C_3S - C_2S -X are heated to about 1600 deg., the liquid is at point W. If lines were drawn from W to the C_3S and C_2S points, the triangle so formed could be treated in the same manner as the triangle C_3S - C_2S -E to indicate percentages of liquid. The quantity of liquid is proportional to the potential C_3A , as at 1455 deg., but the proportionality factor is larger. There is nothing in this case to indicate that undesirable effects will be encountered through raising the temperature to increase the degree of fusion.

In the case of mixtures in the triangle C_3S - C_3A -X, Fig. 7, the liquid follows the boundary between the C_3S and C_3A primary phase regions, starting at E, when the temperature rises above 1455 deg. Referring to Fig. 4, it is seen that this boundary is short, and that at 1470 deg. another invariant point, D, is encountered. At this point CaO, C_3S and C_3A may exist in equilibrium with the liquid. The rela-

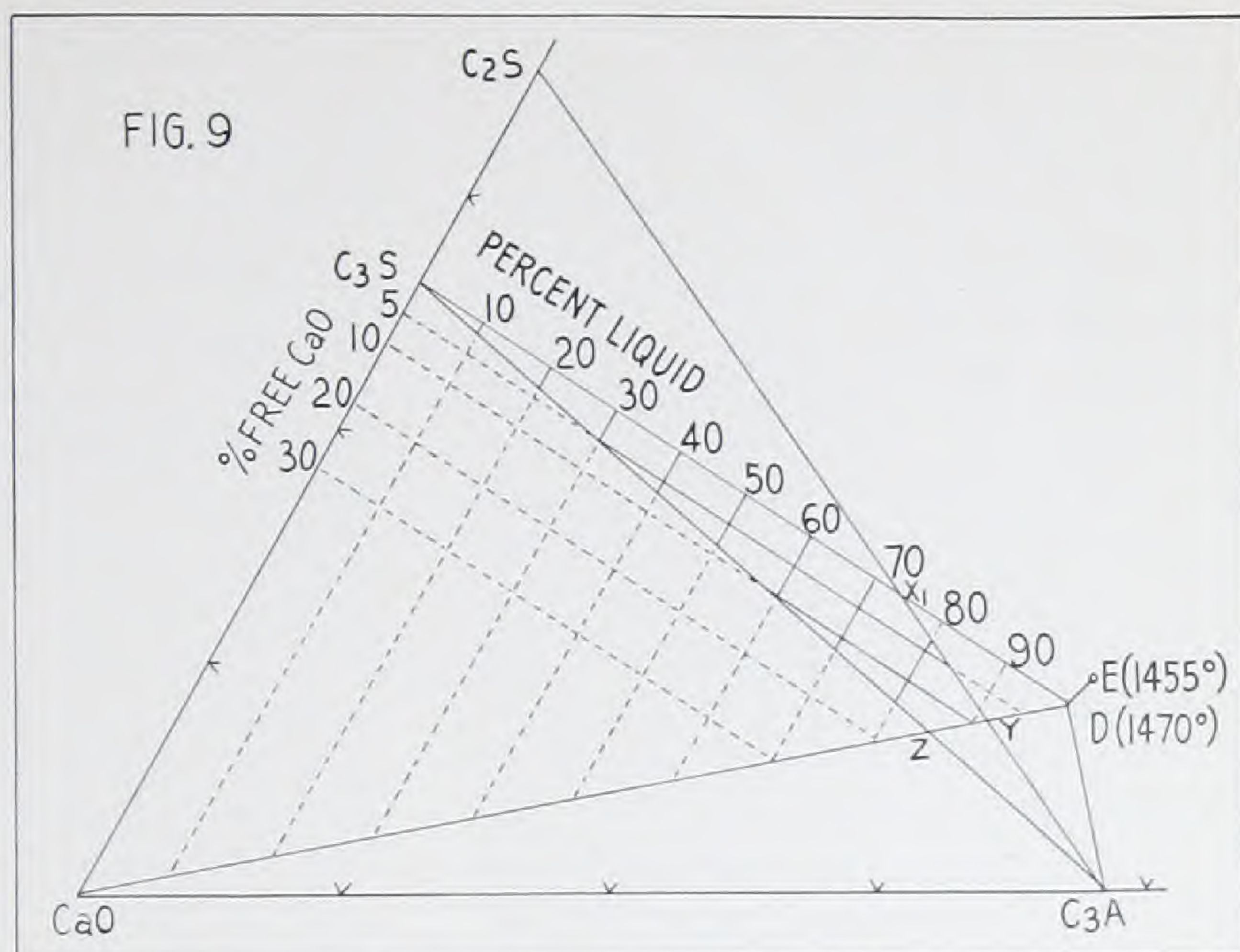
tion between composition and percent liquid when the liquid arrives at D (minimum heat content at 1470 deg.) is shown in Fig. 8. The triangle C_3S - C_3A -D is narrower than triangle C_3S - C_2A -E, Fig. 7, but is similar in the fact that the potential C_2S governs the quantity of liquid. A different situation appears when the heat content at 1470 deg. is a maximum.

Liquid D is capable of existing in equilibrium with solid CaO, C_3S and C_3A . There are four combinations of these phases in groups of three, as follows:

1. C_3S - C_3A -liquid D
2. CaO- C_3S - C_3A
3. CaO- C_3S -liquid D
4. CaO- C_3A -liquid D

Combination 1 has just been considered, and refers to minimum heat content at 1470 deg. Combination 2 also refers to minimum heat content, but only for mixtures in the system CaO- C_3S - C_3A , which crystallize completely at 1470 deg. Combinations 3 and 4 refer to maximum heat content. This may be seen by examining Fig. 3. It may be seen from the fact that, starting at D on the boundary between the CaO and C_3S primary phase regions or on the boundary between the CaO and C_3A regions, the temperature rises.

Fig. 9: Percent liquid and free CaO at 1470 deg. (max. heat content)



Combinations 3 and 4 are represented by the corresponding triangles in Fig. 9. Triangle CaO-C₃A-D will not be discussed, since the portion of the system C₃S-C₂S-C₃A which it includes is of no interest in relation to portland cement. The triangle CaO-C₃S-D includes considerable area in addition to that in the system C₃S-C₂S-C₃A. Since the portion in that system is of particular interest, the lines referring to percentages of liquid D and free CaO are solid lines in the triangle C₃S-C₂S-C₃A, and broken lines outside of that triangle.

In Fig. 9, lines are drawn parallel to the side CaO-C₃S to indicate 10 percent intervals in percentage of liquid D. Since potential percentages of C₃A may also be represented by lines parallel to the same line, as in Fig. 5, the quantity of liquid is proportional to the potential C₃A. This is a decided change from the conditions at minimum heat content at the same temperature. The quadrilateral C₃S-X₁-Y-Z, Fig. 9 (maximum heat content) is a part of the triangle C₃S-C₃A-X₁, in Fig. 8 (minimum heat content), in which the quantity of liquid is proportional to the potential C₂S.

It was shown in our study of Fig. 7 that for ternary cement mixtures of low potential C₂S, at the lowest clinkering temperature, 1455 deg., the percent of liquid is proportional to the

potential C₂S. This is shown by the closely spaced lines in that figure. The small increase of 1.2 percent in the proportion of limestone in passing from F to G is accompanied by a decrease in liquid content about 20 percent to zero. Close control of proportions of raw materials would be required to secure an adequate degree of fusion at this low clinkering temperature. Since high potential C₃S and a corresponding low potential C₂S are sought in the manufacture of high-early-strength cement, it is of interest to consider the effect of raising the temperature of burning. As the temperature of low C₂S ternary mixtures is raised from 1455 deg. to 1470 deg., the liquid passes from E to D, Fig. 4. When the liquid arrives at D, the percent of liquid is still proportional to the potential C₂S, as shown in Fig. 8. However, the lines representing percent liquid are more closely spaced than in Fig. 7, so that for any given composition in the low C₂S range the percent liquid is about 1.3 times as great as at 1455 deg. With further application of heat, there is a substantial increase in percent of liquid without change of temperature, as shown in Fig. 9. However, the advantage of a higher liquid content is offset by the fact that free CaO is present as an equilibrium phase. The percentages of free CaO are represented in Fig. 9

by lines parallel with the C_3S -D line. Since free CaO is an equilibrium phase in that region, it will remain present as long as the temperature is maintained at 1470 deg. and if no heat is withdrawn. It may be noted that the CaO- C_3S boundary in Fig. 4 from point D to the intersection with the 1700 deg. isotherm is nearly straight and practically coincident with a straight line from the C_3S point to D. The percent of free CaO present as an equilibrium phase in low C_2S compositions, therefore does not change to any great extent when the temperature is raised from 1470 deg. to 1700 deg. The free CaO present at equilibrium at or above 1470 deg. will disappear only as the temperature is reduced below 1470 deg., but with practical rates of cooling such as would be possible in a rotary kiln the reduction of free CaO content is likely to be negligible. The best way of avoiding this situation is to maintain compositions on the low CaO side of the C_3S -D line. Ternary compositions on the high CaO side may be burned to a low free CaO content by maintaining temperatures between 1455 deg. and slightly below 1470 deg. for a sufficient period of time.

In the ternary system CaO- Al_2O_3 - SiO_2 , the CaO primary phase region extends outside of the triangle CaO- C_3S - C_3A , and is partly in the triangle C_3S - C_2S - C_3A . It is this condition which makes it possible for free CaO to be an equilibrium phase in ternary portland cement mixtures under some conditions, as has been described. A similar situation exists in the case of the quaternary system CaO- Al_2O_3 - SiO_2 - Fe_2O_3 , as reported by Lea and Parker^{7, 8} in which the CaO primary phase volume extends outside of the tetrahedron CaO- C_3S - C_3A - C_4AF . A similar situation appears in Swayze's report⁹ of the system CaO- Al_2O_3 - SiO_2 - Fe_2O_3 as modified by magnesia, in which the CaO primary phase volume extends outside of the tetrahedron CaO- C_3S - C_3A - C_6A_2F . It consequently appears that the presence of free CaO as an equilibrium phase may be expect-

ed when burning commercial portland cement raw mixtures of low potential C_2S content, as has been found in the ternary system CaO- Al_2O_3 - SiO_2 .

It has been shown in the discussion of Fig. 5 that the line C_3S - C_3A is the theoretical lime limit. All compositions between that line and the CaO vertex contain CaO in excess of the amount necessary to form C_3S and C_3A . This places a limit upon the amount of CaO which can be present in a ternary cement mixture. From the foregoing study of the presence of free CaO as an equilibrium phase in low C_2S mixtures, when burned at high temperatures, it may be seen that there is another kind of lime limit, representing a lime content which should not be exceeded if free CaO as an equilibrium phase is to be avoided.

An investigation by Spohn¹¹ had for its purpose the establishment of the "lime limit" of portland cement. The compositions of mixtures at the lime limit found by Spohn were located on the line C_3S -D. This lime limit was termed the "technical lime limit" by Spohn, to distinguish it from the theoretical lime limit, which is the line C_3S - C_3A . The equation of the line is:

$$CaO = 2.80 SiO_2 + 1.18 Al_2O_3 \quad (18)$$

Lea and Parker⁸ have examined their data on the quaternary system CaO- Al_2O_3 - SiO_2 - Fe_2O_3 with reference to a technical lime limit in that system on a basis similar to Spohn's technical lime limit. Their solution of the problem, which is in harmony with Spohn's remarks on the quaternary system, is that the lime limit in the quaternary system is represented by a plane passing through the C_3S and C_4AF points and through point D. The equation of the plane is:

$$CaO = 2.80 SiO_2 + 1.18 Al_2O_3 + 0.65 Fe_2O_3 \quad (19)$$

Since minor constituents of portland cement are not represented in the equation, it can only represent approximately the technical lime limit in commercial portland cement clinker.

Lea and Parker define the lime "saturation factor" of a cement clink-

er as the ratio of the actual CaO content to the technical lime limit, as found by substitution in equation 19. The saturation factor of a cement may be found similarly, if the CaO derived from gypsum, that is, 0.70 times the percent SO_3 , is deducted from the total CaO. Instead of this ratio, we prefer to calculate the "lime deficiency," which is the amount by which the CaO content falls short of the technical lime limit. This may be found by substitution in the following equation, obtained by transposing terms in equation 19, as follows:

$$\text{L.D.} = 2.80 \text{ SiO}_2 + 1.18 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3 - \text{CaO} \quad (20)$$

in which L.D. represents the lime deficiency.

Since the plane represented by equation 19 passes through the C_3S and C_4AF points in the space model, an equation in terms of potential composition will not involve these compounds. The equation corresponding to equation 20 is as follows:

$$\text{L.D.} = 0.33 \text{ C}_2\text{S} - 0.18 \text{ C}_3\text{A} \quad (21)$$

To avoid exceeding the technical lime limit, the lime deficiency calculated by substitution in equation 20 or 21 should be positive. The lime deficiency to be sought in plant operation will depend upon such conditions as fineness of the raw mix, thoroughness of mixing, and the degree of precision in composition control.

Equations 19-21 are subject to modification when required by future investigations of the quaternary system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3$ and of systems involving additional components. However, they agree quite well with experience, and may serve a useful purpose until more precise relations are formulated.

This paper has been concerned with application of phase equilibrium data to the process of burning portland cement clinker. The phase diagram of the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ involves only three of the oxides in portland cement. It nevertheless has been possible to learn from it some of the principles pertaining to the burning process. Further investigation of

the quaternary system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-Fe}_2\text{O}_3$ will yield much more information. Because of the solid solution series $\text{C}_2\text{F-C}_6\text{A}_2\text{F}$ discovered by Swayze⁹ some details needed for mathematical treatment of that system must be obtained. This introduces difficulties in interpretation not found in the ternary system. The problems concerned with the process of burning cement clinker and with the constitution of portland cement are much more complex than were foreseen when Rankin and Wright investigated the ternary system.

It should be understood from the foregoing study that the changes in character and proportions of phases during the burning process play an important part in determining the character and proportions of phases in the cooled product; that is, the chemical constitution of a cement clinker of any given composition is governed by the treatment it undergoes in the burning and cooling operation. Reducing conditions occasionally exist in a cement kiln, but it will be assumed here that the time-temperature curve is the only governing factor. At clinkering temperatures the clinker is partially fused; that is, it contains liquid. It is sometimes thought that combination of the oxides to form compounds occurs at this stage, and that all that is necessary to secure "complete combination" is to maintain a sufficiently high temperature for a sufficiently long time. This is a misconception. If a given clinkering temperature is maintained until a state of equilibrium exists, one or more cement compounds will be absent, and a liquid will be present. There may be a tendency to assume that the absent compounds are in the liquid but this assumption is not sound. The atomic arrangement in the liquid is haphazard, so that the liquid can not be regarded as being composed of the cement compounds as such. In a paper on the constitution of glass, Morey¹² expresses the situation as follows: "The existence of certain compounds as the stable products of crystalliza-

tion of a liquid is no evidence that they exist as such in the liquid, and no knowledge we have at present permits the identification of any compounds existing in the liquid state."

Following the burning operation, the clinker may be cooled so rapidly that crystallization cannot occur. The liquid then hardens to a glass. The glass, like the liquid, is not composed of cement compounds. The only sound reason for estimating the potential compound composition of glass in clinker is to determine the approximate quantity of each compound which is *not* present as a result of failure of the liquid to crystallize. The quantities of the compounds actually present may then be found by difference. It should be clear that the cooling operation plays an important part in fixing the chemical constitution of cement clinker. In fact, if a mixture of any given composition is maintained at a clinkering temperature until equilibrium is attained, the subsequent cooling operation governs the chemical constitution of the finished product.

It has been the purpose of this paper to use the phase diagram of the ternary system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ as a basis for demonstrating the manner in which a phase diagram may be applied in dealing with problems pertaining to the manufacture of portland cement, and to a study of the chemical constitution of the product. Chemists in direct contact with the manufacture of cement will find it helpful to become familiar with the subject.

Summary

Some of the principles pertaining to the interpretation of phase diagrams have been applied to the phase diagram of the system $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$, with the purpose of gaining an understanding of the clinkering operation. It has been found that:

1. In the process of fusion, liquid is formed at the expense of the solid phases present. The process may continue until one of the solid phases dis-

appears. The percentage of that phase in the potential composition of the mixture governs the percent of liquid.

2. As the proportion of limestone in the raw mix is increased, a point is reached at which C_2S becomes the disappearing phase. The effect of increasing lime content in lowering the percent of liquid becomes very large, so that burning becomes increasingly difficult.

3. The "technical lime limit" is the maximum CaO content which may be maintained without encountering free CaO as an equilibrium phase. This technical, or practical, lime limit is expressed by the equation,

$$\text{CaO} = 2.80 \text{ SiO}_2 + 1.18 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3$$

4. When the technical lime limit is exceeded, the free lime present as an equilibrium phase is not removed by prolonged burning, or by increasing the temperature, but can disappear only by extremely slow cooling.

5. The ideal state represented by the potential compound composition is attained only as a result of extremely slow cooling. If equilibrium is attained at a high temperature, the cooling operation determines the chemical nature of the product.

Study of the phase diagram involving only the three major components of portland cement has brought out some principles which are helpful in understanding the chemistry of the burning operation. Further investigations of systems involving the minor components may be expected to yield more precise knowledge of what goes on in the kiln.

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